Case 1:23-cv-01278-EAW Document 1-7 Filed 12/08/23 Page 1 of 10

Exhibit 7



US009434639B2

(12) United States Patent

Signer-Apel et al.

(10) Patent No.: US 9,434,639 B2

(45) **Date of Patent:** Sep. 6, 2016

(54) LITHIUM SILICATE MATERIALS

(71) Applicant: Ivoclar Vivadent AG, Schaan (LI)

(72) Inventors: Elke Signer-Apel, Oberschan (CH);

Wolfram Höland, Schaan (LI); Marcel Schweiger, Chur (CH); Christian Ritzberger, Nenzing (AT); Harald Bürke, Frastanz (AT); Volker Rheinberger, Vaduz (LI)

(73) Assignee: Ivoclar Vivadent AG, Schaan (LI)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

(21) Appl. No.: 14/567,173

(22) Filed: Dec. 11, 2014

(65) **Prior Publication Data**

US 2015/0094197 A1 Apr. 2, 2015

Related U.S. Application Data

(60) Continuation of application No. 13/940,362, filed on Jul. 12, 2013, now Pat. No. 8,940,651, which is a continuation of application No. 13/175,370, filed on Jul. 1, 2011, now Pat. No. 8,546,280, which is a continuation of application No. 12/944,578, filed on Nov. 11, 2010, now Pat. No. 7,993,137, which is a continuation of application No. 12/253,437, filed on Oct. 17, 2008, now Pat. No. 7,871,948, which is a division of application No. 11/348,053, filed on Feb. 6, 2006, now Pat. No. 7,452,836.

(30) Foreign Application Priority Data

Feb. 8, 2005	(EP)	 	05002588
Jun. 20, 2005	(DE)	 10 200	05 028 637

(51)	Int. Cl.	
` /	C03C 10/04	(2006.01)
	C03C 10/00	(2006.01)
	C03B 32/02	(2006.01)
	C03C 4/00	(2006.01)
	A61C 5/10	(2006.01)
	A61C 13/00	(2006.01)
	A61K 6/027	(2006.01)
	A61K 6/00	(2006.01)
	A61K 6/02	(2006.01)
	A61C 5/08	(2006.01)
	A61C 8/00	(2006.01)
	A61C 13/08	(2006.01)
	A61C 13/083	(2006.01)
	C01B 33/32	(2006.01)
(52)	U.S. Cl.	

6/0273 (2013.01); C01B 33/32 (2013.01); C03B 32/02 (2013.01); C03C 4/0021 (2013.01); C03C 10/0045 (2013.01); C03C 10/0054 (2013.01); C03C 2204/00 (2013.01); Y10T 83/04 (2015.04); Y10T 409/303752 (2015.01)

(58) Field of Classification Search

CPC C03C 10/0027; C03C 10/0018; C03C

10/0009

USPC 501/5, 6, 7, 63, 64, 68, 69, 70; 106/35 See application file for complete search history.

(56) References Cited

U.S. PATENT DOCUMENTS

2,684,911 A 7/1954	
3,022,180 A 2/1962	
3,252,778 A 5/1966	Goodmann et al.
3,287,201 A 11/1966	Chisholm et al.
3,006,775 A 10/1969	Chen
3,679,464 A 7/1972	P. Eppler
3,804,608 A 4/1974	Gaskell et al.
3,816,704 A 6/1974	Borom et al.
3,977,857 A 8/1976	6 Mattox
4,155,888 A 5/1979	Mooth et al.
4,189,325 A 2/1980) Barrett et al.
4,414,282 A * 11/1983	3 McCollister C03C 27/046
	428/433
4,473,653 A 9/1984	l Rudoi
4,480,044 A * 10/1984	McAlinn C03C 10/00
	501/4
4,515,634 A 5/1985	Wu et al.
4,671,770 A 6/1987	Bell et al.
(C-	
(Co	ntinued)

FOREIGN PATENT DOCUMENTS

CA	2252660	5/1999
DE	1696473	8/1970
	(Cor	ntinued)

OTHER PUBLICATIONS

Kalinina et al. Crystallization Products of Lithium Silicate Glasses. The Structure of Glass, vol. 3: Catalyzed Crystallization of Glass. Authorized translation from the Russian by E. B. Uvarov, B. Sc., A.R.C.S., D.I.C., A.R.I.C. Consultants Bureau Enterprises, Inc, 1964. pp. 53-64.*

(Continued)

Primary Examiner — Noah Wiese (74) Attorney, Agent, or Firm — Hodgson Russ LLP

(57) ABSTRACT

Lithium silicate materials are described which can be easily processed by machining to dental products without undue wear of the tools and which subsequently can be converted into lithium silicate products showing high strength.

9 Claims, No Drawings

Page 2

U.S. PATENT DOCUMENTS 475,488 A 1/1988 Nagashims 470,5348 A 1/1989 Colored at 2008 012094 At 52008 Selweiger et al. 470,5348 A 1/1989 Colored at 2008 012094 At 52008 At 52008 Colored at 2009 00214 At 52008 A	(56)		Referen	ces Cited		2006/0082 2006/0257			Hauptmann et al. Pfeiffer et al.	
4,755,488 A 7,1988 Nagashima		U.S	S. PATENT	DOCUMENTS						
4.998.536 A 101999 Cyokou et al. 2008.0198823 Al 12009 Billinet et al. 4.99171 A 121990 Hornsouchi et al. 2009.00023737 Al 120090 Carlot et al. 2009.00023737 Al 102090 Carlot et al. 2009.00023737 Al 2009.00023										
A97114 A 121999 Formachier tal A97114 A 121990 Formachier tal A97114 A 121990 Formachier tal A97114 A 121990 Formachier tal A97114 A12990 A94ct al A97114 A97114 A12990 A98ct al A97114								5/2008 8/2008	Schweiger et al.	
4.977,114 A 121990 Infrinouchi et al. 2009/0038834 Al 2.2009 Apel et al.		, ,								
S.176.961 A										
5,176,961 A 11993 Crooker et al. 2009.0256774 Al 10/2009 Castillo 5,217,573 A 61993 Beall et al. 2019.0256778 Al 10/2009 Castillo 5,472,130 A 7,1995 Reall et al. 2019.00528778 Al 10/2009 Castillo 5,472,130 A 7,1995 Reall et al. 2019.00528778 Al 10/2009 Castillo 5,472,130 A 7,1995 Reinberger et al. 2019.0054864 Al 2011.0054806 5,678,563 A 5,1997 Nonyel 2012.0054888 Al 6/2012 Castillo 5,691,266 A 11997 Taguchi et al. 2012.024864 Al 10/2012 Rizberger et al. 5,691,266 A 11997 Taguchi et al. 2012.024864 Al 10/2012 Rizberger et al. 5,691,267 A 11998 Alone et al. 2012.034806 Al 1997 Deschang et al. 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 1997 5,707,777 A 11998 Alone et al. 2012.034806 Al 2012.03480	:	5,045,402 A	* 9/1991							
\$217.378		5 17C 0C1 A	1/1002		3/472					
S. 1979 A 6 1993 Beall et al. 2010 0083706 Al. 4 2010 Castillo										
5.432,130 A 7,1995 Rheinberger et al. 2011/03/649 Al 10/2011 Rizberger et al. 5.607.81 A 41996 Perincrew 2011/03/649 Al 10/2011 Rizberger et al. 5.608.13 A 5.608.43 A 5.1999 Venget et al. 5.608.43 A 5.1999 Perincrew 5.707,777 A 11998 Aoait et al. 5.608.019 A 11/1997 Finals. et al. 5.608.019 A 11/1997 Perincrew 5.707,777 A 11998 Aoait et al. 5.608.019 A 11/1997 Perincrew 5.707,777 A 11998 Aoait et al. 5.608.019 A 11/1997 Perincrew 5.707,777 A 11998 Aoait et al. 5.608.019 A 11/1994 A 11/1994 Aoait et al. 5.608.019 A 11/1994 A 11/1994 A 11/1994 A 11/1994 A 1										
5,618,763 A 41907 Frank et al. 2012/094822 Al. 42012 Castillo 5,681,286 A 51907 Neryel 2012/0148898 Al 62012 Castillo 5,681,286 A 11/1907 Frank et al. 2012/0348642 Al. 10/2012 Durschang et al. 2012/0348642 Al. 2012/0348644 Al. 2012/0348642 Al. 2012/0348642 Al. 2012/0348644 Al. 2012/0348642	:	5,432,130 A								
5,632,564 A 5,1997 Nenyel 2012/0148988 Al 6,2012 Rizberger et al. 5,691,256 A 7,61997 Taguchi et al. 5,698,482 A 12/1997 Frank et al. 5,698,482 A 12/1997 Frank et al. 5,702,514 A 12/1997 Frank et al. 5,702,514 A 12/1997 Petricrew 5,707,777 A 12/1998 Aoai et al. 5,908,856 A 12/1999 Wang DE 2451121 5/1975 5,908,856 A 10/1999 Schweiger et al. 5,908,856 A 10/1999 Schweiger et al. 6,048,859 A 2/2000 Parcent et al. 6,048,859 A 2/2000 Struki 6,050,858 A 2/2000 Struki 6,193,958 A 2/2000 Struki 6										
5,641,347 A 11/1997 Tagschi et al. 2012/030607 Al 12/2012 Durschang et al. 5,698,492 A 12/1997 Frank ct al. 5,698,492 A 12/1997 Frank FOREIGN PATENT DOCUMENTS 5,707,777 A 11/1998 Acad et al. DE 245/1121 5/1975 S. 5,707,777 A 11/1998 Acad et al. DE 3015/529 6/1988 S. 5,703,777 A 11/1998 Acad et al. DE 3015/529 6/1988 S. 5,703,777 A 11/1998 Acad et al. DE 1957/5794 6/1998 S. 5,938,939 A 8/1999 Wang DE 4/1994 S. 5,938,939 A 8/1999 Wang DE 1957/5794 6/1996 6/1996 6/1998 Bag 1998 S. 5,938,939 A 8/1999 Wang DE 1957/5794 6/1996										
S.098.401			6/1997	Grabowski et al.						
5,084,812 A 12/1997 Petticrew FOREIGN PATENT DOCUMENTS						2012/0309	607 A1	12/2012	Durschang et al.	
5,702,514 A 12/1997 Aoai et al. DE 2451121 5/1975 5,872,069 A Aoai et al. DE 3015529 6/1980 5,874,376 A 2/1999 Aoai et al. DE 2495619 11/1980 5,973,879 A 2/1999 Aoai et al. DE 2495619 11/1980 5,973,879 A 2/1999 Shiweiger et al. DE 9750794 6/1996 6,022,819 A 2/2000 Sizzuki EP 031737 3/1998 6,048,589 A 2/2000 Sizzuki EP 031737 3/1998 6,095,682 A 8/2000 Sizzuki EP 031737 3/1998 6,095,682 A 8/2000 Real et al. EP 536479 4/1993 6,095,682 A 8/2000 Real et al. EP 631672 4/1993 6,095,682 A 8/2000 Telakheni et al. EP 681797 4/1993 6,119,483 A 9/2000 Telakheni et al. EP 681797 4/1993 6,121,775 A 9/2000 Drescher et al. EP 681797 4/1993 6,141,775 A 9/2000 Drescher et al. EP 67147433 6/2000 6,163,000 A 12/2000 Bartusch et al. EP 112764 8/2001 6,163,000 A 12/2000 Bartusch et al. EP 112764 8/2001 6,163,000 A 12/2000 Bartusch et al. EP 115764 8/2001 6,247,076 Bl 8/2001 Zychek EP 1505041 2/2005 6,257,076 Bl 8/2001 Abe et al. GB 752243 7/1956 6,287,671 Bl 9/2001 Guiot et al. P 325080 8/1933 6,342,458 Bl 1/2002 Schweiger et al. P 325080 8/1933 6,342,458 Bl 1/2002 Schweiger et al. P 9/1074418 3/1999 6,441,346 Bl 8/2002 Petiterew P 9/1074318 3/1999 6,441,346 Bl 8/2002 Petiterew P 9/1074418 3/1999 6,441,346 Bl 8/2002 Petiterew P 9/1074418 3/1999 6,517,62,38 B2 1/2004 Bordkin et al. P 20008323 3/2005 6,802,898 B2 1/2004 Bordkin et al. P 20008325 1/2004 6,802,898 B2 1/2002 Schweiger et al. P 200083154 1/2003 6,802,898 B2 1/2002 Schweiger et al. P 200083154 1/2003 6,903,003,003,003,003,003,003,003,003,003							EODEIG	NI DATEI	NT DOCUMENT	c
5,872,076 A 21999 Abe DE 3015529 61980 5,874,376 A 21999 Taguchi et al. DE 2949619 11/1980 5,978,959 A 81999 Wang DE 2949619 11/1980 5,978,959 A 81999 Wang DE 19750794 61/1995 5,978,958 A 81999 Wang DE 19750794 61/1995 6,082,819 A 22000 Enrare et al. DE 19750794 61/1998 6,082,819 A 22000 Enrare et al. DE 19647730 31/1998 6,082,819 A 22000 Enrare et al. DE 19647730 31/1998 6,082,819 A 22000 Enrare et al. DE 19647730 31/1998 6,082,819 A 22000 Enrare et al. DE 19647730 31/1998 6,106,747 A 82000 Wohlwend EP 336472 41/193 6,119,747 A 82000 Wohlwend EP 0817597 11/1998 6,121,775 A 9/2000 Drescher et al. EP 0817597 11/1998 6,121,175 A 9/2000 Drescher et al. EP 774933 6/2000 6,1474,827 B 11/2001 Goto EP 112564 8/2001 6,1474,827 B 11/2001 Goto EP 1422210 5/2004 6,252,202 B1 6/2001 Zychek EP 1505041 2/2005 6,267,505 B1 7/2001 Ginuz EP 1688898 8/2006 6,270,876 B1 8/2001 Frank et al. GB 752243 7/1956 6,280,803 B1 8/2001 Frank et al. GB 284655 6/1995 6,280,803 B1 8/2001 Frank et al. GB 284655 6/1995 6,280,803 B1 8/2001 Frank et al. GB 284655 6/1995 6,481,303 B1 8/2001 Frank et al. GB 284655 6/1995 6,481,303 B1 22002 Schweiger et al. PP 315080 8/1933 6,481,303 B1 22002 Schweiger et al. PP 1174418 3/1999 6,514,803 B1 22002 Schweiger et al. PP 1174418 3/1999 6,514,803 B1 22003 Schweiger et al. PP 1174418 3/1999 6,514,803 B1 22003 Schweiger et al. PP 1174418 3/1999 6,517,623 B1 22002 Schweiger et al. PP 200058877 12/2001 6,803,873 B1 22003 Schweiger et al. PP 200058877 12/2001 6,803,873 B1 22003 Schweiger et al. PP 200058877 12/2001 6,803,873 B1 22003 Schweiger et al. WO 2000412802 27 on the crystallization and properties of lithium disilicate glasses. Journal of Material Science 1966, 1.269-2000030502 Al 22002 Schweiger et al. WO 200000000 Al 1/2002 Schweiger et al. WO 2000000000 Al 1/2							TOKEIO.	NIAID	NI DOCOMENI	
S.874,376 A 2/1999 Wang DE 2949619 11/1980						DE	2451	121	5/1975	
5.938,859 A 8/1999 Schweiger et al. DE 1975/0794 6/1996 6.022,819 A 2/2000 Panzera et al. DE 1964/739 3/1998 8/1997 6.064,8589 A 4/2000 Strukik EP 031773 8/1987 6.066,584 A 5/2000 Hollander EP 536479 4/1993 6/106,747 A 8/2000 Hollander EP 536479 4/1993 6/106,747 A 8/2000 Hollander EP 536479 4/1993 6/106,747 A 8/2000 Takahashi et al. EP 0817597 1/1998 6/121,175 A 9/2000 Drescher et al. EP 0817597 1/1998 6/121,175 A 9/2000 Bizzio EP 1175/64 8/2001 6/157/004 A 1/2/200 Bizzio EP 1175/64 8/2001 6/157/004 A 1/2/200 Bizzio EP 1175/64 8/2001 6/157/004 A 1/2/200 Bizzio EP 115/004 1/2/2005 6/257/057 B 17/201 Goto EP 142/210 5/2004 6/257/057 B 17/201 Goto EP 142/210 5/2004 6/257/057 B 17/201 Goto EP 142/210 5/2004 6/257/057 B 17/201 Goto EP 15/05/041 2/2005 6/267/057 B 17/201 Goto EP 16/05/041 2/2005 6/267/057 B 17/201 Goto EP 16/05/041 2/2005 6/287/121 B1 9/201 Goto EP 16/05/041 2/2005 6/287/121 B1 9/201 Goto EP 16/05/041 2/2005 6/287/121 B1 9/201 Goto EP 16/05/041 2/2005 6/287/058 B1 / 2/201 Schweiger et al. PP 30/208846 8/1993 6/202 Schweiger et al. PP 30/208846 8/1993 6/202 Schweiger et al. PP 10/208836 8/1993 6/202 Schweiger et al. PP 10/208837 10/2004 8/2005 Schweiger et al. PP 10/208837 10/2005 10/203 Schweiger et al. PP 2001/28807 10/203 Schweiger et al. PP 2001/28807 10/203 10/203 Schweiger et al. PP 2001/										
5,968,856 A 10/1999 Schweiger et al. DE 1975/0794 6,1996 6,042,858 A 2/000 Panzera et al. DE 1964/7739 3,1998 6,048,589 A 2/000 Krell et al. EP 0,231773 8,1987 6,095,682 A 8/2000 Krell et al. EP 536479 4,1993 6,105,747 A 8/2000 Wohlwend EP 0,817597 1,1998 6,119,483 A 2/2000 Drescher et al. EP 0,827941 3,1998 6,121,715 A 9/2000 Drescher et al. EP 0,827941 3,1998 6,121,715 A 9/2000 Drescher et al. EP 7,74933 6,2000 6,157,004 A 12/2000 Bartusch et al. EP 11,7564 8,2001 6,163,020 A 12/2000 Bartusch et al. EP 11,7564 8,2001 6,174,827 B1 1/2001 Grot EP 11,7564 8,2001 6,174,827 B1 1/2001 Grot EP 14,22210 5,2004 6,252,020 B1 6/2001 Zychek EP 16,88398 8,2006 6,270,876 B1 8/2001 Frank et al. GB 7,2243 7,1956 6,288,043 B1 8/2001 Guiot et al. P 3,5080 8,1953 6,342,458 B1 1/2002 Schweiger et al. P 5094017 10,1974 6,455,451 B1 9/2002 Schweiger et al. P 5094017 10,1974 6,441,346 B1 8/2002 Zychek A61K 6,033 P 1011409 4,1998 6,531,623 B1 2/2003 Schweiger et al. P 11,74418 3,1999 6,531,623 B1 2/2003 Schweiger et al. P 11,74418 3,1999 6,531,623 B1 2/2003 Schweiger et al. P 10,200,23334 1,1999 6,531,623 B1 2/2003 Schweiger et al. P 2001,288027 10,2001 6,818,573 B2 1/2004 Brotkin et al. P 2001,288027 10,2001 6,818,573 B2 1/2004 Brotkin et al. P 2001,288027 10,2001 6,818,573 B2 1/2001 Schweiger et al. WO 20,200,200,300,300 A1 2/2002 Schweiger et al. WO 20,200,300,300 A1 2/2002 Coto et al. P 20,000,300,300 A1 2/2002 Coto et al. WO 20,200,300,300 A1 2/2002 Coto et al. P 20,000,300,300 A1 2/2002 Coto et al. WO 20,200,300,300 A1 2/2002 Coto et al. WO 20,200,300,300 A1 2/200 Coto et al. WO 20,200,300,300 A1 2/2002 Coto										
6.048,159 A 2/2000 Suzuki EP 031773 31998 6.0484,589 A 4/2000 Suzuki EP 031773 81987 6.066,584 A 5/2000 Krell et al. EP 536479 41993 6.106,747 A 8/2000 Hollander EP 536479 41993 6.106,747 A 8/2000 Hollander EP 536479 41993 6.119,748 A 9/2000 Takahashi et al. EP 0817597 11998 6.121,175 A 9/2000 Drescher et al. EP 0817597 11998 6.121,175 A 9/2000 Bizzio EP 174933 62000 6.157,004 A 12/2000 Bizzio EP 117564 82001 6.163,020 A 12/2000 Bizzio EP 117564 82001 6.163,020 A 12/2000 Bizzio EP 1152641 11/2001 6.174,827 B1 1/201 Goto EP 1422210 5/2004 6.252,202 B1 6/2001 Zychek EP 1505041 2/2005 6.267,0375 B1 7/201 Gratz EP 1688398 8/2006 6.270,876 B1 8/2001 Frank et al. GB 752243 71956 6.288,038 B1 8/201 Abe et al. GB 752243 71956 6.288,038 B1 8/201 Frank et al. GB 284655 61995 6.287,121 B1 9/2001 Giuti et al. GB 284655 61995 6.324,348 B1 1/2002 Schweiger et al. PP 3325080 8/1953 6.441,346 B1 8/2002 Schweiger et al. PP 195004017 10174 6.450,238 B2 7/2002 Schweiger et al. PP 195004017 10174 6.451,461 B1 8/2002 Schweiger et al. PP 195004017 10174 6.451,463 B1 8/2002 Schweiger et al. PP 195004017 10174 6.452,328 B1 1/2002 Schweiger et al. PP 195004017 10174 6.453,481 B1 2/2003 Schweiger et al. PP 195004017 101794 6.451,463 B1 8/2002 Schweiger et al. PP 195004017 101974 6.451,463 B1 8/2002 Schweiger et al. PP 195004017 101974 6.451,463 B1 8/2002 Schweiger et al. PP 195004017 101995 6.451,463 B1 1/2004 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2004 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 11/2001 Brockin et al. PP 2001288027 102001 6.453,473 B2 1/2001 Brockin et al. PP 2001288027 102001 6.453,474 B2 1/2002 Brockin et al. PP 2001288027 102001 6.453,474 B2 1/2002 Brockin et al. PP 2001288027 102001 6.453,474 B1 1/2002 Brockin et al.			10/1999	Schweiger et al.						
6,096,584 A \$ 52000 Hollander EP \$36479 4/1993 6,095,582 A \$ 82000 Hollander EP \$36572 4/1993 6,106,747 A \$ 82000 Wohlwend EP \$0817597 1/1998 6,119,175 A \$ 92000 Descher et al. EP \$0827941 3/1998 6,121,175 A \$ 92000 Descher et al. EP \$774933 6/2000 6,163,020 A \$ 12/2001 Bizzio EP \$173641 11/2001 6,163,020 A \$ 12/2001 Goto EP \$1125641 11/2001 6,174,827 B1 1/201 Goto EP \$150641 12/2005 6,267,959 B1 7/201 Gratz EP \$150641 2/2005 6,270,876 B1 8/2001 Abe et al. GB \$72243 7/1956 6,287,121 B1 9/2001 Gioti et al. GB \$752243 7/1956 6,287,121 B1 9/2001 Gioti et al. JP \$325080 8/1953 6,342,485 B1 1/2002 Schweiger et al. JP \$325080 8/1953 6,443,346 B1 8/2002 Eychck JP \$178710 7/1995 6,441,346 B1 8/2002 Schweiger et al. JP \$1032354 12/1998 6,514,833 B1 2/2003 Schweiger et al. JP \$1032354 12/1998	(6,022,819 A	2/2000	Panzera et al.						
6,095,682 A 82000 Hollander EP 536572 4/1993 6,119,483 A 9,2000 Wolhwend EP 0817597 1/1998 6,112,175 A 9,2000 Drescher et al. EP 0827941 3/1998 6,121,175 A 9,2000 Drescher et al. EP 74933 6/2000 6,157,004 A 12,2000 Birusch et al. EP 1127564 8,2001 6,163,020 A 12,2000 Bartusch et al. EP 1127564 8,2001 6,163,020 A 12,2000 Bartusch et al. EP 1127564 8,2001 6,174,827 B1 1,2001 Goto EP 142,210 5,2004 6,252,202 B1 6,2001 Zychek EP 150,5041 2,2005 6,267,0376 B1 8,2001 Abe et al. GB 75,243 7,1956 6,270,376 B1 8,2001 Abe et al. GB 75,243 7,1956 6,289,863 B1 8,2001 Guiot et al. JP 32,0800 8,1933 6,342,438 B1 1,2002 Schweiger et al. JP 50,90417 10,1974 6,376,397 B1 8,2002 Zychek JP 7,1956 6,441,346 B1 8,2002 Zychek JP 7,1956 6,441,346 B1 8,2002 Zychek JP 7,1956 6,445,541 B1* 9,2002 Brodkin										
6.196,747 A 82000 Wohlwend EP 0817597 11998 6.121,175 A 92000 Takahashi et al. EP 0827941 31998 6.121,175 A 92000 Drescher et al. EP 774933 62000 6.163,020 A 122000 Bartusch et al. EP 1127564 82001 6.163,020 A 122001 Got EP 1127564 82001 6.262,202 Bl 62001 Zychek EP 1152564 112001 6.252,202 Bl 62001 Zychek EP 1505041 22005 6.267,595 Bl 72001 Gratz EP 1505041 22005 6.267,595 Bl 72001 Gratz EP 1505041 22005 6.270,876 Bl 82001 Abe et al. GB 752243 7,1956 6.280,836 Bl 82001 Abe et al. GB 752243 7,1956 6.287,121 Bl 92001 Guiot et al. JP 325080 81953 6.342,458 Bl 12002 Schweiger et al. JP 325080 81953 6.440,348 Bl 12002 Schweiger et al. JP 3508046 81993 6.445,451 Bl * 92002 Zychek JP 9501092 2,1997 6.445,451 Bl * 92002 Zychek JP 9501092 2,1997 6.455,451 Bl * 92003 Schweiger et al. JP 1174418 3,1999 6.517,623 Bl 22003 Schweiger et al. JP 1174418 3,1999 6.517,623 Bl 22003 Schweiger et al. JP 11074418 3,1999 6.517,623 Bl 22004 Brodkin et al. JP 200053375 Bl 72004 Brodkin et al. JP 200053325 Al 12009 Schweiger et al. JP 200053325 Al 12009 Schweiger et al. JP 200053376 3,2005 7,162,23 Bl 22001 Brodkin et al. JP 200053376 3,2005 7,162,548 Bl 12001 Schweiger et al. JP 200053776 3,2005 7,162,548 Bl 12000 Schweiger et al. JP 200053776 3,2005 7,162,548 Bl 12000 Schweiger et al. WO 9512678 121995 7,452,586 Bl 22010 Brodkin et al. JP 200053776 3,2005 7,867,930 Bl 12011 Apel et al. WO 9512678 121995 7,867,930 Bl 12011 Schweiger et al. WO 90053776 3,2005 7,867,930 Bl 12011 Schweiger et al. WO 9007028787 121995 7,867,930 Bl 12011 Schweiger et al. WO 9007028787 121995 8,444,756 Bl 52011 Schweiger et al. WO 9007028780 6,2007, 27, 1571-1577. Jan. 1, 1907. McMillan et al., The Structure and Properties of Hibium disilicate glasses, Journal of Non-Crystalline Solids 1993, 163, 1,12, Jan. 1, 1907. McMillan et al., The Glasse-Ceramic Society, 2007, 27, 1571-1577. Jan. 1, 1906.										
6.119,483 A 9,2000 Takahashi et al. EP 0827941 3/1998 6.121,175 A 9,2000 Drescher et al. EP 774933 3/1998 6.157,004 A 12,2000 Bizzio EP 112,7664 8,2001 6.163,004 A 12,2000 Bizzio EP 112,7664 8,2001 6.174,827 B1 1,2001 Grot EP 14,22210 5,2004 6.252,202 B1 6,2001 Zychek EP 1,505041 2,2005 6.267,595 B1 7,2001 Gratz EP 1,688,398 8,2006 6.270,376 B1 8,2001 Abe et al. GB 75,224 7,1956 6.280,863 B1 8,2001 Frank et al. GB 75,224 7,1956 6.280,863 B1 8,2001 Schweiger et al. JP 3,208,405 6,1995 6.342,458 B1 1,2002 Schweiger et al. JP 3,208,406 8,1953 6.420,288 B2 7,2002 Schweiger et al. JP 5,094017 10,1974 6.376,397 B1 4,2002 Petticrew JP 0,500,8846 8,1993 6.441,346 B1 8,2002 Zychek JP 7,187710 7,1995 6.441,346 B1 8,2002 Zychek JP 7,187710 7,1995 6.441,346 B1 8,2002 Schweiger et al. JP 7,187710 7,1995 6.485,849 B2 11/2002 Petticrew JP 9,501,092 2,1997 6.514,893 B1 2,2003 Schweiger et al. JP 11074418 3,1999 6.514,893 B1 2,2003 Schweiger et al. JP 113,14938 11/1999 6.514,623 B1 2,2003 Brodkin et al. JP 113,14938 11/1999 6.517,623 B1 2,2004 Brodkin et al. JP 113,14938 11/1999 6.518,573 B2 11/2004 Brodkin et al. JP 2000,28802 3,2005 7,166,548 B2 12,007 Abel et al. WO 9,232,678 12/1995 7,452,836 B2 11/2008 Schweiger et al. WO 9,332,678 12/1995 7,452,836 B2 11/2001 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,237,676 3,2005 7,166,548 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger et al. WO 9,232,678 12/1995 7,452,836 B2 11/2010 Schweiger e		, ,								
6,157,004 A 12/200 Bizzio EP 1127564 8/2001 6,174,827 Bl 1/2001 Goto EP 1422210 5/2004 6/252,202 Bl 6/2001 Zychek EP 15/2041 11/2001 6/267,595 Bl 7/2001 Gratz EP 1688398 8/2006 6/267,595 Bl 8/2001 Abe et al. GB 752243 7/1956 6/287,121 Bl 9/2001 Gratz EP 1688398 8/2006 6/270,876 Bl 8/2001 Frank et al. GB 752243 7/1956 6/287,121 Bl 9/2001 Gratic et al. JP 3/25080 8/1953 6/342,458 Bl 1/2002 Schweiger et al. JP 3/25080 8/1953 6/342,458 Bl 1/2002 Schweiger et al. JP 9/201092 2/1997 6/455,451 Bl 9/2002 Brodkin et al. JP 9/201092 2/1997 6/455,451 Bl 9/2002 Brodkin et al. JP 11074418 3/1999 6/207,237 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6/207,238 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6/207,238 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6/207,238 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6/207,238 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6/207,238 Bl 2/2003 Schweiger et al. JP 20013847 2/2001 6/808,2894 Bl 1/2002 4/2003 4/2004 4/20							0827	941	3/1998	
6,163,020 A 12/2001 Bartusch et al. 6,174,827 Bl 1/2001 Goto EP 1422210 5/2004 6,252,202 Bl 6/2001 Zychek EP 150,5041 2/2005 6,267,595 Bl 7/2001 Gratz EP 1688398 8/2006 6,270,876 Bl 8/2001 Frank et al. GB 752243 7/1956 6,280,863 Bl 8/2001 Frank et al. GB 2284655 6/1995 6,287,121 Bl 9/2001 Guiot et al. JP 350,800 8/1953 6,342,458 Bl 1/2002 Schweiger et al. JP 50,904017 10/1974 6,376,397 Bl 4/2002 Peticrew JP 505,00417 10/1974 6,451,436 Bl 8/2002 Zychek JP 9,501,002 2/1997 6,441,346 Bl 8/2002 Zychek JP 9,501,002 2/1997 6,451,436 Bl 8/2002 Zychek JP 106/35 JP 103,233,354 12/1998 6,514,839 Bl 2/2003 Schweiger et al. JP 113,449,84 11/1999 6,514,839 Bl 2/2003 Schweiger et al. JP 113,449,84 11/1999 6,514,623 Bl 2/2003 Schweiger et al. JP 113,449,84 11/1999 6,514,537 Bl 1/2004 Peticrew JP 117,4418 3/1999 6,503,257 Bl 7/2003 Nagata JP 2001035,417 2/2001 6,802,894 B2 10/2004 Brodkin et al. JP 113,493,84 11/199 6,514,623 Bl 2/2003 Schweiger et al. JP 2001038,257 Bl 7/2003 Nagata JP 2001038,257 Bl 7/2003 Nagata JP 2001038,17 2/2001 6,818,573 B2 11/2004 Peticrew JP 2001038,17 2/2001 6,802,894 B2 10/2003 Brodkin et al. JP 2001038,17 2/2001 6,802,894 B2 10/2004 Brodkin et al. JP 2001038,17 2/2001 6,803,373 B1 2/2007 Schweiger et al. JP 2001038,17 2/2001 6,803,373 B1 2/2007 Schweiger et al. WO 200704046 4/2006 7,805,586 B1 2/2007 Schweiger et al. WO 200704046 4/2006 7,807,903,137 B2 2/201 Resident al. WO 200704046 4/2006 7,807										
6.174.827 Bl 1/2001 Goto EP 1422210 5.2004 6.262.202 Bl 6/2001 Zychek EP 1505041 2.2005 6.267.958 Bl 7/2001 Gratz EP 1688398 8.2006 6.270.876 Bl 8/2001 Frank et al. GB 752243 7/1956 6.280.863 Bl 8/2001 Frank et al. GB 752245 7/1956 6.287.121 Bl 9/2001 Guiot et al. JP 325080 8/1953 6.342.488 Bl 1/2002 Schweiger et al. JP 3050801 10/1974 6.376.397 Bl 4/2002 Petticrew JP 65008846 8/1993 6.440.348 Bl 2/2002 Schweiger et al. JP 5094017 10/1974 6.455.451 Bl 9/2002 Foodkin A61K 6/033 JP 10101409 4/1998 6.441.346 Bl 8/2002 Zychek JP 5051092 2/1997 6.445.4541 Bl 9/2002 Petticrew JP 6501092 2/1997 6.485.849 B2 II/2002 Petticrew JP 10/14418 3/1999 6.514.893 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6.514.623 Bl 2/2003 Schweiger et al. JP 11074418 3/1999 6.514.623 Bl 2/2003 Brodkin et al. JP 10074381 1/1999 6.514.638 B2 I/2004 Petticrew JP 2001035417 2/2001 6.818.573 B2 II/2004 Petticrew JP 2001035417 2/2001 6.818.573 B2 II/2004 Petticrew JP 2001035417 2/2001 6.818.573 B2 II/2004 Petticrew JP 200062832 3/2005 7.166.488 B2 I/2007 Apel et al. JP 2000553776 3/2005 7.166.488 B2 I/2007 Apel et al. JP 2008515549 5/2008 7.452.836 B2 II/2008 Apel et al. WO 0228802 4/2002 7.655.586 B1 2/2010 Brodkin et al. WO 0247616 6/2002 7.866.933 B2 I/2011 Apel et al. WO 2000040464 4/2006 7.867.933 B2 I/2011 Apel et al. WO 2000040464 4/2006 7.867.933 B2 I/2011 Schweiger et al. WO 20000400060 8.444.756 B2 Schweiger et al. WO 20000400060 8.444.756 B2 Schweiger et al. WO 20000030514 1/2003 7.867.933 B2 I/2011 Schweiger et al. WO 200000000000000000000000000000000000										
6.267,595 Bl 7,2001 Gratz EP 1688398 8/2006 6.270,876 Bl 8/2001 Abe et al. GB 752243 7/1956 6.280,863 Bl 8/2001 Frank et al. GB 752243 7/1956 6.287,876 Bl 8/2001 Frank et al. GB 752243 7/1956 6.287,121 Bl 9/2001 Guit et al. JP 325080 8/1953 6.342,458 Bl 1/2002 Schweiger et al. JP 5094017 10/1974 6.376,397 Bl 4/2002 Petticrew JP 5094017 10/1974 6.376,397 Bl 4/2002 Zychek JP 9501092 2/1997 6.445,451 Bl 8/2002 Zychek JP 9501092 2/1997 6.445,451 Bl 8/2002 Zychek JP 9501092 2/1997 6.455,451 Bl 8/2002 Schweiger et al. JP 10101409 4/1998 6.485,849 B2 11/2002 Petticrew JP 106/35 JP 10323354 1/21998 6.514,893 Bl 1/2002 Schweiger et al. JP 1174418 3/1999 6.517,623 Bl 2/2003 Brodkin et al. JP 11074418 3/1999 6.503,257 Bl 7/2003 Agata JP 2001035417 2/2001 6.802,894 B2 10/2004 Brodkin et al. JP 2001288027 10/2001 6.818,573 B2 11/2004 Petticrew JP 200062832 3/2005 7.166,548 B2 1/2007 Apel et al. JP 2001355476 3/2005 7.166,548 B2 1/2007 Apel et al. JP 200855776 3/2005 7.166,548 B2 1/2007 Apel et al. JP 200855776 3/2005 7.452,836 B2 1/2008 Apel et al. WO 93352678 12/1995 7.452,836 B2 1/2008 Apel et al. WO 9335014 1/2003 7.806,694 B2 10/2010 Brodkin et al. WO 0247616 6/2002 7.806,694 B2 10/2010 Brodkin et al. WO 0247616 6/2002 7.806,694 B2 10/2010 Schweiger et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 7.807,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 7.807,933 B2 2/2011 Apel et al. WO 2007028787 3/2007 7.807,933 B2 2/2011 Apel et al. WO 2007028787 3/2007 7.807,933 B2 2/2011 Apel et al. WO 2007028787 3/2007 7.807,933 B2 2/										
6.270.876 Bl 8.2001 Fank et al. 6.280.863 Bl 8.2001 Fank et al. 6.287.121 Bl 9.2001 Guiot et al. 6.287.121 Bl 9.2001 Guiot et al. 6.376.397 Bl 4.2002 Petticrew JP 50.94017 10/1974 6.4376.397 Bl 4.2002 Petticrew JP 50.94017 10/1974 6.440.288 B2 7.2002 Schweiger et al. JP 7187710 7/1995 6.441.346 Bl 8.2002 Zychek JP 95.01092 2/1997 6.455.451 Bl* 9.2002 Brodkin										
6.288,636 Bl 8/2001 Frank et al. 6.287,121 Bl 9/2001 Giuci et al. 6.342,458 Bl 1/2002 Schweiger et al. 9.7001 Schweiger et al. 9.7002 Schweiger et al. 9.7002 Schweiger et al. 9.7002 Schweiger et al. 9.7003 Schweiger et al. 9.7003 Schweiger et al. 9.7004 Schweiger et al. 9.7005 Schweiger et al. 9.7005 Schweiger et al. 9.7005 Schweiger et al. 9.7006 Schweiger et al. 9.7006 Schweiger et al. 9.7007 Schweiger et al. 9.7008 Schweiger et al. 9.7009 Schweiger et al.										
6.287,121 Bl 9/2001 Guiot et al. 6.342,488 Bl 1/2002 Schweiger et al. 9										
6.376,397 Bl 4/2002 Petticrew JP 05208846 8/1993 6.420,288 B2 7/2002 Schweiger et al. JP 7187710 7/1995 6.441,346 Bl 8/2002 Zychek JP 9501092 2/1997 6.455,451 Bl 8 9/2002 Brodkin						JP				
6.420,288 B2 7/2002 Schweiger et al. JP 7187710 7/1995 6,4453,451 B1* 9/2002 Brodkin										
6,441,346 B1			7/2002	Schweiger et al.						
106/35 JP 10323354 12/1998			8/2002	Zychek						
6.485,849 B2 11/2002 Petticrew 6.514,893 B1 2/2003 Schweiger et al. JP 11074418 3/1999 6.517,623 B1 2/2003 Brodkin et al. JP 11074418 3/1999 6.593,257 B1 7/2003 Nagata JP 2001035417 2/2001 6.802,894 B2 10/2004 Brodkin et al. JP 2001035417 2/2001 6.818,573 B2 11/2004 Petticrew JP 200062832 3/2005 7,162,321 B2 1/2007 Luthard et al. JP 200553776 3/2005 7,166,548 B2 1/2007 Apel et al. JP 200553776 3/2005 7,166,548 B2 1/2007 Apel et al. JP 200553776 3/2005 7,316,740 B2 1/2008 Schweiger et al. WO 9532678 12/1995 7,452,836 B2 11/2008 Apel et al. WO 0228802 4/2002 7,655,586 B1 2/2010 Brodkin et al. WO 0247616 6/2002 7,880,694 B2 10/2010 Brodkin et al. WO 03035014 1/2003 7,816,291 B2 10/2010 Schweiger et al. WO 2006042046 4/2006 7,867,930 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,867,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,867,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,867,933 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 20070028787 3/2007 MeMillan et al., Influence of Zr02 on the crystallization and properties of lithium disilicate glass-ceramic Society, 2007, 27, 1571-1577. Jan. 1, 2007. MeMillan et al., The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic, Journal of Material Science 1966, I. 269-279, Jan. 1, 1996. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-	(6,455,451 B1	* 9/2002							
6,514,893 B1 2/2003 Schweiger et al. JP 11074418 3/1999 (5,517,623 B1 2/2003 Brodkin et al. JP 11314938 11/1999 (5,503,257 B1 7/2003 Nagata JP 2001035417 2/2001 (6,802,894 B2 10/2004 Brodkin et al. JP 2001035417 2/2001 (6,802,894 B2 10/2004 Petticrew JP 200062832 3/2005 (7,162,321 B2 1/2007 Luthardt et al. JP 2000535776 3/2005 (7,166,548 B2 1/2007 Luthardt et al. JP 200553776 3/2005 (7,166,548 B2 1/2007 Apel et al. JP 200553776 3/2005 (7,452,836 B2 1/2008 Schweiger et al. WO 9532678 12/1995 (7,452,836 B2 11/2008 Apel et al. WO 028802 4/2002 (7,655,586 B1 2/2010 Brodkin et al. WO 0247616 6/2002 (7,655,586 B1 2/2010 Brodkin et al. WO 0247616 6/2002 (7,866,949 B2 10/2010 Schweiger et al. WO 03035014 1/2003 (7,867,933 B2 1/2011 Apel et al. WO 2006042046 4/2006 (7,867,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 (7,892,995 B2 2/2011 Castillo (7,993,137 B2 8/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012143137 10/2012 (7,871,948 B2 1/2014 Apel et al. WO 2012	,	6 485 840 B2	11/2002		06/35					
6,517,623 B1 2/2003 Brodkin et al. JP 1314938 11/1999 6,593,257 B1 7/2003 Nagata JP 2001035417 2/2001 6,802,894 B2 10/2004 Brodkin et al. JP 2001288027 10/2001 6,818,573 B2 11/2004 Petticrew JP 200062832 3/2005 7,162,321 B2 1/2007 Luthardt et al. JP 200553776 3/2005 7,166,548 B2 1/2007 Apel et al. JP 200553776 3/2005 7,316,740 B2 1/2008 Schweiger et al. WO 9532678 12/1995 7,452,836 B2 11/2008 Brodkin et al. WO 0228802 4/2002 7,655,586 B1 2/2010 Brodkin et al. WO 024802 4/2002 7,806,694 B2 10/2010 Brodkin et al. WO 03035014 1/2003 7,816,291 B2 10/2010 Schweiger et al. WO 2006042046 4/2006 7,867,930 B2 1/2011 Apel et al. WO 2006042046 4/2006 7,867,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Schweiger et al. Solveiger										
6,802,894 B2 10/2004 Brodkin et al. 6,818,573 B2 11/2004 Petticrew JP 200052832 3/2005 7,166,548 B2 1/2007 Apel et al. 7,166,548 B2 1/2007 Apel et al. 7,166,548 B2 1/2008 Schweiger et al. 7,166,548 B2 1/2008 Apel et al. 8,06,694 B2 10/2010 Brodkin et al. 8,06,694 B2 10/2010 Brodkin et al. 8,06,694 B2 10/2010 Schweiger et al. 8,06,693 B2 1/2011 Apel et al. 8,042,358 B2 1/2011 Apel et al. 8,042,358 B2 1/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,047,021 B2 1/2011 Schweiger et al. 8,047,021 B2 1/2011 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,040,0006174 A1 7/2001 Brennan 1/2002 Schweiger et al. 8,040,00061674 A1 7/2002 Schweiger et al. 8,040,0006174 A1 7/2002 Schweiger et al. 8,040,0000600 A1 1/2002 Schweiger et al. 8,040,0006174 A1 7/2001 Schweiger et al. 8,040,0006174 A1 7/2002 Sch	(6,517,623 B1	2/2003	Brodkin et al.		JР			11/1999	
6,818,573 B2 11/2004 Petticrew 7,162,321 B2 1/2007 Apel et al. 7,166,548 B2 1/2008 Apel et al. 7,316,740 B2 1/2008 Schweiger et al. 7,452,836 B2 11/2008 Apel et al. 7,452,836 B2 11/2008 Apel et al. 7,805,694 B2 10/2010 Brodkin et al. 7,806,694 B2 10/2010 Brodkin et al. 7,806,694 B2 10/2010 Schweiger et al. 7,807,930 B2 11/2011 Apel et al. 7,867,933 B2 1/2011 Apel et al. 7,867,933 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Apel et al. 7,892,995 B2 2/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,042,358 B2 10/2011 Schweiger et al. 8,042,358 B2 10/2011 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,047,021 B2 11/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,041,021 B2 11/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,041,035 B2 11/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,041,035 B2 11/2011 Schweiger et al. 8,042,358 B2 10/2011 Schweiger et al.										
7,162,321 B2										
7,166,548 B2 1/2007 Apel et al. 7,316,740 B2 1/2008 Schweiger et al. WO 9532678 12/1995 7,452,836 B2 11/2008 Apel et al. WO 0228802 4/2002 7,655,586 B1 2/2010 Brodkin et al. WO 0247616 6/2002 7,806,694 B2 10/2010 Brodkin et al. WO 03035014 1/2003 7,816,291 B2 10/2010 Schweiger et al. WO 2006042046 4/2006 7,867,930 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,867,933 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,867,933 B2 1/2011 Apel et al. WO 2012143137 10/2012 7,871,948 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Castillo 7,993,137 B2 8/2011 Castillo 8,047,021 B2 11/2011 Schweiger et al. 8,042,358 B2 10/2011 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 8,444,756 B2 5/2013 Brennan 2001/0006174 A1 7/2001 Brennan 2002/0010063 A1 1/2002 Schweiger et al. 2002/0010063 A1 1/2002 Schweiger et al. 2002/0012563 A1 2/2002 Schweiger et al. 2002/0031670 A1 3/2002 Goto et al. 2002/0031670 A1 3/2002 Goto et al. 2002/00318238 A1 9/2004 Lambrecht Schweiger						JP				
7,452,836 B2 11/2008 Apel et al. 7,655,868 B1 2/2010 Brodkin et al. WO 0247616 6/2002 7,806,694 B2 10/2010 Brodkin et al. WO 03035014 1/2003 7,816,291 B2 10/2010 Schweiger et al. WO 2006042046 4/2006 7,867,930 B2 1/2011 Apel et al. WO 2007028787 3/2007 7,871,948 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Castillo 7,892,995 B2 2/2011 Castillo 8,042,358 B2 10/2011 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,047,021 B2 11/2012 Schweiger et al. 8,047,021 B2 11/2013 Schweiger et al. 8,047,021 B2 11/2013 Schweiger et al. 8,047,021 B2 11/2013 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,041,756 B2 5/2013 Schweiger et al. 8,041,756 B2 5/2013 Schweiger et al. 9,041/4006 42006 Apel et al., Influence of Zr02 on the crystallization and properties of lithium disilicate glass-ceramics derived from multi-component system, Journal of European Ceramic Society, 2007, 27, 1571-1577. Jan. 1, 2007. McMillan et al., The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic, Journal of Material Science 1966, I. 269-279. Jan. 1, 1966. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-	,	7,166,548 B2	1/2007			JP	2008515	549	5/2008	
7,655,586 B1 2/2010 Brodkin et al. 7,806,694 B2 10/2010 Brodkin et al. 7,816,291 B2 10/2010 Schweiger et al. 7,867,930 B2 1/2011 Apel et al. 7,867,933 B2 1/2011 Apel et al. 7,871,948 B2 1/2011 Apel et al. 7,893,137 B2 2/2011 Castillo 7,993,137 B2 8/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 2001/0006174 A1 7/2001 Brennan 2002/0009600 A1 1/2002 Peng 2002/0010063 A1 1/2002 Schweiger et al. 2002/0031670 A1 3/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht 2005/0098064 A1* 5/2005 Schweiger										
7,806,694 B2 10/2010 Brodkin et al. 7,816,291 B2 10/2010 Schweiger et al. 7,867,930 B2 1/2011 Apel et al. 7,867,933 B2 1/2011 Apel et al. 7,871,948 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Castillo 7,993,137 B2 8/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,042,358 B2 10/2011 Schweiger et al. 8,044,756 B2 5/2013 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 2001/0006174 A1 7/2001 Bronan Schweiger et al. 2002/0032653 A1 1/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2003/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht Schweiger et al. 2005/0098064 A1* 5/2005 Schweiger et al. 2006/035025 A1 3/2002 Schweiger et al. 2007/035025 A1 3/2002 Schweiger et al. 2008/035025 A1 3/2002 Schweiger et al. 2008/035025 A1 3/2002 Schweiger et al. 2008/035025 A1 3/2002 Schweiger et al. 2009/										
7,867,930 B2 1/2011 Apel et al. 7,867,933 B2 1/2011 Apel et al. 7,871,948 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Castillo 7,993,137 B2 8/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,047,021 B2 11/2012 Schweiger et al. 9,001/0006174 A1 7/2001 Brennan Schweiger et al. 2001/0006163 A1 1/2002 Peng Schweiger et al. 2002/0032563 A1 2/2002 Schweiger et al. 2002/0031670 A1 3/2002 Goto et al. 2002/0035025 A1 3/2002 Goto et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht Schweiger			10/2010	Brodkin et al.						
7,867,933 B2 1/2011 Apel et al. 7,871,948 B2 1/2011 Apel et al. 7,892,995 B2 2/2011 Castillo 7,993,137 B2 8/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. 8,047,021 B2 11/2011 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 8,444,756 B2 5/2013 Schweiger et al. 2001/0006174 A1 7/2001 Brennan 2002/0009600 A1 1/2002 Peng Schweiger et al. 2002/0035025 A1 2/2002 Schweiger et al. 2002/0035025 A1 3/2002 Goto et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht Schweiger										
7,871,948 B2										
7,993,137 B2 8/2011 Apel et al. 8,042,358 B2 10/2011 Schweiger et al. Schweiger et al. Apel et al., Influence of Zr02 on the crystallization and properties of lithium disilicate glass-ceramics derived from multi-component system, Journal of European Ceramic Society, 2007, 27, 1571-1577. 2001/0006174 A1 7/2001 Brennan system, Journal of European Ceramic Society, 2007, 27, 1571-1577. 2002/0010063 A1 1/2002 Schweiger et al. McMillan et al., The Structure and Properties of a Lithium Zinc 2002/0031670 A1 3/2002 Goto et al. Schweiger et al. Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. Deubener et al., Influence of Zr02 on the crystallization and properties of lithium disilicate glass-ceramics derived from multi-component system, Journal of European Ceramic Society, 2007, 27, 1571-1577. Jan. 1, 2007. McMillan et al., The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic, Journal of Material Science 1966, I. 269-279. Jan. 1, 1966. 2002/0031670 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht Deubener et al., Influence of Zr02 on the crystallization and properties of lithium disilicate glass-ceramic Society, 2007, 27, 1571-157						WO				
8,042,358 B2							OTF	HER PU	BLICATIONS	
8,047,021 B2						Anel et al	Influence o	f ZrO2 or	the crystallization	and properties
8,444,756 B2 5/2013 Schweiger et al. 2001/0006174 A1 7/2001 Brennan 1/2002 Peng 1/2002/0010063 A1 1/2002 Schweiger et al. 2002/0010063 A1 1/2002 Schweiger et al. 2002/0022563 A1 2/2002 Schweiger et al. 2002/0031670 A1 3/2002 Goto et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht 2005/0098064 A1* 5/2005 Schweiger C03C 10/0027 106/35 Schweiger C03C 10/0027 Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-						-			•	
2001/0009600 A1 1/2002 Brenan 1/2002 Peng Jan. 1, 2007. McMillan et al., The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic, Journal of Material Science 1966, I. 269-2002/0035025 A1 3/2002 Goto et al. 279. Jan. 1, 1966. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline 2005/0098064 A1* 5/2005 Schweiger	;	8,444,756 B2	5/2013	Schweiger et al.			_			
2002/0010063 A1 1/2002 Schweiger et al. 2002/0022563 A1 2/2002 Schweiger et al. 2002/0031670 A1 3/2002 Goto et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht 2005/0098064 A1* 5/2005 Schweiger C03C 10/0027 106/35 McMillan et al., The Structure and Properties of a Lithium Zinc Silicate Glass-Ceramic, Journal of Material Science 1966, I. 269-279. Jan. 1, 1966. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-						-		,		,
2002/0031670 A1 3/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2002/0035025 A1 3/2002 Schweiger et al. 2004/0182538 A1 9/2004 Lambrecht 2005/0098064 A1* 5/2005 Schweiger C03C 10/0027 106/35 Schweiger C03C 10/0027 106/35 Schweiger et al., Glass-Ceramic, Journal of Material Science 1966, I. 269-279. Jan. 1, 1966. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-								Structure	and Properties of a	Lithium Zinc
2002/0031670 A1 3/2002 Goto et al. 279. Jan. 1, 1966. 2002/0035025 A1 3/2002 Schweiger et al. Deubener et al., Induction time analysis of nucleation and crystal grown in di- and metasilicate glasses, Journal of Non-Crystalline 2005/0098064 A1* 5/2005 Schweiger										
2004/0182538 A1 9/2004 Lambrecht grown in di- and metasilicate glasses, Journal of Non-Crystalline 2005/0098064 A1* 5/2005 Schweiger C03C 10/0027 Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-			3/2002	Goto et al.				. ,.		
2005/0098064 A1* 5/2005 Schweiger C03C 10/0027 Solids 1993, 163, 1-12. Jan. 1, 1993. Holand et al., Glass-ceramic technology, American Chemical Soci-				-						
Holand et al., Glass-ceramic technology, American Chemical Soci-					0027					on-Crystamne
	2003	, 505000T AI	5,2005							hemical Soci-
	2005	5/0127544 A1	6/2005							

Page 3

(56) References Cited

OTHER PUBLICATIONS

Holand et al., Control of nucleation in glass ceramics, Phil. Trans. Soc. Lond. A 2003, 361, 575-589. Jan. 1, 2003.

Holand et al., Principles and phenomena of bioengineering with glass-ceramics of dental restoration, Journal of the Europaen Ceramics Society 2007, 27, 1571-1577. Jan. 1, 2007.

Ivoclar Vivadent, Inc., IPS e.max lithium disilicate, 627329, Rev. Feb. 2009. Feb. 1, 2009.

Durschang, Report of Results, Fraunhofer Institute for Silicate Research ISC Glass and Mineral Materials, 2015. Jan. 1, 2015. Stookey, S.D., "Chemical Machining of Photosensitive Glass," Ind. Eng. Chem. 45:115-118 (1993). Jan. 1, 1993.

Montedo et al., Low Thermal Expansion Sintered LZSA Glass Ceramics, American Ceramic Society Bulletin, vol. 87, Issue 7, pp. 34-40. Jul. 1, 2008.

Von Clausburch et al., "The effect of P205 on the Crystallization and Microstructure of Glass-Ceramics in the Si02—Li02—K2O—ZnO—P2O5 System," J. of Non-Crystalline Solids 263&264, pp. 388-394 (2000). Jan. 1, 2000o

Giassi et al., "Injection Moulding of LiO2—ZrO2—SiO2—Al2O3 (LZSA) Glass Ceramics," Glass Technol., 46(3), 277-280 (2005). Jan. 1, 2005.

Borom, et al., "Strength and Microstructure in Lithium Disilicate Glass Ceramics," J. Am. Ceram. Soc. 58 (9-10): 285-391 (1975). Jan. 1, 1975.

de Oliveira et al., "Sintering and Crystalization of a Glass Powder in the Li2O—ZrO2—SiO2 System," J. Am. Ceramic Soc. 81(3):777-780 (1998). Jan. 1, 1998.

Von Clausburch et al., "Effect of ZnO on the Crystallization, Microstructure, and Properties of Glass-Ceramics in the

SiO2=Li2O—K2O—P2O5 System," Glastech. Ber. Glass. Sci. Technol. 74(8):223-229 (2001). Jan. 1, 2001.

Sundh et al., Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing. Dental Materials (2005) 21, 476-482. Jan. 1, 2005.

Stookey, S.D., "Chemical Machining of Photosensitive Glass," Ind. Eng. Chem. 45:115-118 (1993).

Montedo et al., Low Thermal Expansion Sintered LZSA Glass Ceramics, American Ceramic Society Bulletin, vol. 87, Issue 7, pp. 34-40, 2008.

Von Clausburch et al., "The effect of P205 on the Crystallization and Microstructure of Glass-Ceramics in the Si02—Li02—K2O—ZnO—P205 System," J. of Non-Crystalline Solids 263&264, pp. 388-394 (2000).

Giassi et al., "Injection Moulding of LiO2—ZrO2—SiO2—Al2O3 (LZSA) Glass Ceramics," Glass Technol., 46(3), 277-280 (2005). Borom, et al., "Strength and Microstructure in Lithium Disilicate Glass Ceramics," J. Am. Ceram. Soc. 58 (9-10): 285-391 (1975). de Oliveira et al., "Sintering and Crystalization of a Glass Powder in the Li2O—ZrO2—SiO2 System," J. Am. Ceramic Soc. 81(3):777-780 (1998).

Von Clausburch et al., "Effect of ZnO on the Crystallization, Microstructure, and Properties of Glass-Ceramics in the SiO2=Li2O—K2O—P2O5 System," Glastech. Ber. Glass. Sci. Technol. 74(8):223-229 (2001).

Sundh et al., Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing. Dental Materials (2005) 21, 476-482.

European Search Report for EP Application No. 10171839.3, Jan. 25, 2011.

http://en.wikipedia.org/wiki/Nucleation Sep. 20, 2012.

^{*} cited by examiner

1 LITHIUM SILICATE MATERIALS

This application is a continuation of U.S. application Ser. No. 13/940,362, filed on Jul. 7, 2013, which is a continuation of U.S. application Ser. No. 13/175,370, filed on Jul. 1, 2011, 5 now U.S. Pat. No. 8,546,280, which is a continuation of U.S. application Ser. No. 12/944,578, filed Nov. 11, 2010, now U.S. Pat. No. 7,993,137, which is a continuation of U.S. patent application Ser. No. 12/253,437, filed Oct. 17, 2008, now U.S. Pat. No. 7,871,948, which is a division of U.S. 10 patent application Ser. No. 11/348,053, filed Feb. 6, 2006, now U.S. Pat. No. 7,452,836, which claims priority to European Patent Application Serial No. EP 05002588.1, filed Feb. 8, 2005, and German Patent Application No. 10 2005 028 637.2, filed Jun. 20, 2005, all of which are herein 15 incorporated by reference in their entirety.

FIELD OF THE INVENTION

The invention primarily relates to lithium silicate mate- 20 rials which can be easily shaped by machining and subsequently converted into shaped products with high strength.

BACKGROUND OF THE INVENTION

There is an increasing demand for materials which can be processed into dental restorative products, such as crowns, inlays and bridges, by means of computer controlled milling machines. Such CAD/CAM methods are very attractive as they allow to provide the patient quickly with the desired 30 restoration. A so-called chair-side treatment is thus possible for the dentist.

However, materials suitable for processing via computer aided design/computer aided machining (CAD/CAM) methods have to meet a very specific profile of properties.

First of all, they need to have in the finally prepared restoration appealing optical properties, such as translucence and shade, which imitate the appearance of the natural teeth. They further need to show high strength and chemical durability so that they can take over the function of the 40 natural tooth material and maintain these properties over a sufficient period of time while being permanently in contact with fluids in the oral cavity which can even be aggressive, such as acidic in nature.

Secondly and very importantly, it should be possible to 45 machine them in an easy manner into the desired shape without undue wear of the tools and within short times. This property requires a relatively low strength of the material and is therefore in contrast to the desired properties mentioned above for the final restoration.

The difficulty of combining the properties of low strength in the stage of the material to be processed and a high strength of the final restoration is reflected by the known materials for a CAD/CAM processing which are in particular with respect to an easy machinability unsatisfactory.

DE-A-197 50 794 discloses lithium disilicate glass ceramics which are primarily intended to be shaped to the desired geometry by a hot-pressing process wherein the molten material is pressed in the viscous state. It is also possible for processes. However, it has been shown that the machining of these materials results in a very high wear of the tools and very long processing times. These disadvantages are caused by the high strength and toughness primarily imparted to the materials by the lithium disilicate crystalline phase. Moreover, it has been shown that the machined restorations show only a poor edge strength. The term "edge strength" refers

2

Filed 12/08/23

to the strength of parts of the restoration having only a small thickness in the range of few 1/10 mm.

Further approaches of achieving easy machinability together with a high strength of the final restoration have also been made. EP-B-774 993 and EP-B-817 597 describe ceramic materials on the basis of Al₂O₃ or ZrO₂ which are machined in an unsintered state which is also referred to as "green state". Subsequently, the green bodys are sintered to increase the strength. However, these ceramic materials suffer from a drastical shrinkage of up to 50% by volume (or up to 30% as linear shrinkage) during the final sintering step. This leads to difficulties in preparing the restorations with exactly the dimensions as desired. The substantial shrinkage represents a particular problem if complicated restorations are manufactured, such as a multi-span bridge.

From S. D. Stookey: "Chemical Machining of Photosensitive Glass", Ind. Eng. Chem., 45, 115-118 (1993) and S. D. Stookey: "Photosensitively Opacifiable Glass" US-A-2 684 911 (1954) it is also known that in lithium silicate glass ceramics a metastable phase can be formed at first. For example in photosensitive glass ceramics (Fotoform®, Foto-Ceram®) Ag-particles are formed using UV-light. These Ag-particles serve as crystallization agent in a lithium metasilicate phase. The areas which were exposed to light are in a subsequent step washed out by diluted HF. This procedure is possible since the solubility of the lithium metasilicate phase in HF is much higher than the solubility of the parent glass. The glass portion remaining after said solubilizing process (Fotoform®) can be transferred into a lithium disilicate glass ceramic (FotoCeram®) by an additional heat treatment.

Also investigations of Borom, e.g. M.-P. Borom, A. M. Turkalo, R. H. Doremus: "Strength and Microstructure in Lithium Disilicate Glass-Ceramics", J. Am. Ceram. Soc., 58, No. 9-10, 385-391 (1975) and M.-P. Borom, A. M. Turkalo, R. H. Doremus: "Verfahren zum Herstellen von Glaskeramiken" DE-A-24 51 121 (1974), show that a lithium disilicate glass ceramic can in the first instance crystallize in varying amounts as metastable lithium metasilicate phase. However, there also exist compositions which crystallize in the form of the disilicate phase from the beginning and the metasilicate phase is not present at all. A systematic investigation of this effect has not become known. From the investigations of Borom it is also known that the glass ceramic which contains lithium metasilicate as the main phase has a reduced strength compared to the one of a glass ceramic which only contains a lithium disilicate phase.

It has further been found out that the presence of ZnO in lithium silicate glass ceramics of the prior art is undesirable especially when highly translucent dental restorations are to be produced. Under such circumstances, the strong opalescent effect caused by ZnO is apparent and results in unacceptable optical properties for a restoration which is to 55 imitate the natural tooth material.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to these materials to be shaped by computer aided milling 60 eliminate these disadvantages and in particular to provide a material which can be easily shaped by computer-aided milling and trimming processes and can subsequently be converted into a high-strength dental product which also displays a high chemical durability and excellent optical properties and exhibits a drastically reduced shrinkage during said final conversion, and achieves all these properties without the need for ZnO as a component.

25

3

This object is achieved by the lithium silicate glass ceramic according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

It has surprisingly been shown that by using a starting glass of a very specific composition and a specific process it is possible to provide in particular a glass ceramic which has metastable lithium metasilicate (Li₂SiO₃) as main crystalline phase rather than lithium disilicate (Li₂Si₂O₅). This lithium metasilicate glass ceramic has a low strength and toughness and hence can be easily machined into the shape of even complicated dental restorations, but can after such machining be converted by a heat treatment into a lithium disilicate glass ceramic product with outstanding mechanical properties, excellent optical properties, in particular a strongly reduced opalescence, and very good chemical stability thereby undergoing only a very limited shrinkage.

The lithium silicate glass ceramic according to the invention comprises the following components:

Component	wt%
SiO ₂	64.0-75.0, in particular 64.0-73.0
Li ₂ O	13.0-17.0
K_2O	2.0-5.0
$\overline{\text{Al}_2\text{O}_3}$	0.5-5.0
Nucleating agent	2.0-5.0
Me(II)O	0-3.0

with Me(II)O being selected from at least one of CaO, BaO, MgO and SrO, and comprises less than 0.1 wt. % of ZnO.

It is preferred that the glass ceramic is essentially free of 35

It is surprising that even without presence of ZnO the glass ceramic according to the invention fulfils the mentioned multiple requirements. This was possible by the preferably by the ratios of some of these components to each

Preferred glass ceramics are those which comprise lithium metasilicate as main crystalline phase. Such glass ceramics are also referred to in the following as lithium metasilicate 45 glass ceramics.

It has also been found out to be beneficial if the glass ceramic comprises 0 to 2.0 and preferably 0 to 1.5 wt. % of Me(II)O. Me(II)O is in particular selected from at least one of Cao and MgO. Particularly preferred glass ceramics 50 comprise 0.1 to 1.0 wt. % of MgO.

The nucleating agent is preferably at least one of P_2O_5 and compounds of the elements Pt, Ag, Cu and W. It serves to induce formation of lithium metasilicate crystalls and is preferably P₂O₅.

Further, it was shown that a specific molar ratio of SiO₂ to Li₂O serves to ensure that upon the necessary heat treatment of a corresponding starting glass mainly lithium metasilicate and lithium disilicate, respectively, is produced. This is of particular importance. While a lithium metasilicate 60 glass ceramic essentially free of lithium disilicate results in particular in an excellent machinability, a lithium disilicate restoration essentially free of the easily dissolvable lithium metasilicate has a very good chemical stability.

Thus, it was found preferable that the molar ratio of 65 SiO₂:Li₂O is at least 2.2:1, preferably at least 2.3:1, and most preferred in the range of 2.3:1 to 2.5:1.

4

Moreover, investigations revealed that the molar ratio of Al₂O₃:K₂O is of significance for obtaining the desired tranclucence and the predominant crystallization of lithium metasilicate.

It is preferred that the molar ratio of Al₂O₃:K₂O is in the range of 1:0.5 to 1:2.0 and preferably is from 1:1 to 1:2.0.

There also exist preferred ranges for the amounts of components of the glass ceramic according to the invention. These can be used independently from each other.

It is preferred that the glass ceramic comprises 2.5 to 5.0 wt. % of Al_2O_3 .

It is also preferred that the glass ceramic comprises 70.0 to 73.0 wt. % of SiO₂.

It is also preferred that the glass ceramic comprises 0 to 4.0, preferably 0.1 to 4.0, more preferably 1.0 to 4.0 and most preferred 1.5 to 3.0 wt. % of ZrO₂. If the emphasis is on the achieving of a high strength of the final lithium disilicate ceramic, then 0 to 2.0 wt. % to of ZrO₂ are 20 advantageous.

It is further preferred that the glass ceramic comprises at least one of the following components in an amount of:

Component	wt%
Li ₂ O K ₂ O	14.0-16.0 3.0-4.5
coloring and fluorescent metal oxides	0-7.5, preferably 0.5-3.5.

The metal of the coloring and fluorescent metal oxides is preferably selected from group f-elements and in particular from the group of Ta, Tb, Y, La, Er, Pr, Ce, Ti, V, Fe and Mn. The colouring or fluorescent oxides ensure that the colour of the final dental product matches that of the natural tooth material of the patient in question.

Further, the glass ceramic may comprise as additional component Na₂O in an amount of 0 to 2.0 wt.-%.

Additional components to enhance the technical processselection of the other components and their amounts and 40 ability of the glass may also be present. Such additional components may therefore be in particular compounds such as B₂O₃ and F which in general amount to 0 to 5.0% by weight.

> Generally the amount of lithium metasilicate is 20 to 80 vol.-%. It has surprisingly been shown that a specific volume portion of lithium metasilicate should be present to achieve excellent processing properties. Thus, it is further preferred that the lithium metasilicate crystalline phase forms 20 to 50 vol % and in particular 30 to 40 vol % of the lithium silicate glass ceramic. Such a part of the volume leads to the crystals being present rather remote from each other and hence avoids a too high strength of the glass ceramic.

> If the emphasis is on the achieving of a high strength of the lithium disilicate ceramic, then the lithium metasilicate phase preferably forms more than 50 and up to 80 vol. % of the lithium silicate glass ceramic.

> The lithium metasilicate crystals are preferably of lamellar or platelet form. This leads to a very good machinability of the lithium metasilicate glass ceramic without use of high energy and without uncontrolled breaking. The latter aspect of uncontrolled breaking is for example known from glasses which are generally unsuitable for machining. It is assumed that the preferred morphology of the lithium metasilicate crystals is also responsible for the surprisingly high edge strength of products, e.g. complicated dental restorations, can be made from the lithium metasilicate glass ceramic according to the invention.

The lithium silicate glass ceramic according to the invention preferably is in the form of a blank. The blank usually takes the form of a small cylinder or a rectangular block. The exact form depends on the specific apparatus used for the desired computer-aided machining of the blank.

5

After the machining, the lithium silicate glass ceramic has preferably the shape of a dental restoration, such as an inlay, an onlay, a bridge, an abutment, a facing, a veneer, a facet, a crown, a partial crown, a framework or a coping.

A lithium silicate glass ceramic according to the invention 10 which comprises lithium disilicate as main crystalline phase is a further preferred embodiment of the invention. It is preferred that this lithium disilicate glass ceramic is formed in a process wherein the lithium metasilicate of a glass ceramic according to the invention is converted to lithium 15 disilicate crystals.

A dental product made from lithium disilicate glass ceramic according to the invention is a further preferred embodiment of the invention. It is preferred that such product is formed in a process wherein the lithium meta- 20 silicate of a glass ceramic according to the invention is converted to lithium disilicate crystals.

The lithium metasilicate glass ceramic according to the invention is preferably prepared by a process which com-

- (a) producing a starting glass containing the components of the glass ceramic,
- (b) subjecting the starting glass to a first heat treatment at a first temperature to give a glass product which contains nuclei suitable for forming lithium metasili- 30 cate crystals,
- (c) subjecting the glass product to a second heat treatment at a second temperature which is higher than the first temperature to obtain the lithium silicate glass ceramic with lithium metasilicate as the main crystalline phase. 35

In step (a), usually a melt of a starting glass is produced which contains the components of the glass ceramic. For this purpose a corresponding mixture of suitable starting materials, such as carbonates, oxides, and phosphates, is prepared and heated to temperatures of, in particular 1300 to 1600° 40 C., for 2 to 10 hours. In order to obtain a particularly high degree of homogeneity, the glass melt obtained may be poured into water to form glass granules and the glass granules obtained are melted again.

It is further preferred that the melt of the starting glass is 45 cooled, such as to room temperature, before subjecting it to step (b). The melt of the starting glass is also usually poured into a mould to form a starting glass blank.

In some cases it is convenient to control a cooling procedure such that it not only relaxes the glass, but also 50 effects the first heat treatment of step (b).

In step (b) the starting glass is subjected to a first heat treatment at a first temperature to cause formation of nuclei for lithium metasilicate crystals. Preferably, this first heat treatment comprises heating the starting glass to a tempera- 55 ture of 500 to 600° C. for a period of about 10 minutes to 3 hours. This results in formation of a great number of nuclei that ensure a very satisfactory crystal growth. It also ensures that in the further processing after step (c) to give a lithium disilicate glass ceramic a very homogeneous lithium disili- 60 cate structure can be obtained.

It is also advantageous that the second heat treatment in step (c) comprises heating the glass product to a second temperature of 570° to 750° C., preferably 570 to 670° C., and more preferably to about 650° C.

It has further surprisingly been shown that relatively high temperatures lead to high amounts of lithium metasilicate 6

which in turn lead to a high amount of lithium disilicate in the third heat treatment. Such high amounts of lithium disilicate impart a high strength to the ceramic. Thus, if the emphasis is on the achieving a high strength final product, then it is advantageous to carry out the second heat treatment at 680° to 720° C., and preferably 690° to 710° C. and more preferably about 700° C.

Depending on the specific composition of a selected starting glass, it is possible for the skilled person by means of differential scanning calorimetry (DSC) and x-ray diffraction analyses to determine suitable conditions in steps (b) and (c) to result in glass ceramics having the desired morphology and size of the crystals of lithium metasilicate. Moreover, these analyses allow also the identification of conditions avoiding or limiting the formation of undesirable other crystalline phases, such as of the high-strength lithium disilicate, or of cristobalite and lithium phosphate.

Usually, the starting glass of step (a), the glass product of step (b), or preferably the lithium metasilicate glass ceramic of step (c) is shaped to a desired geometry by machining or by hot pressing. The machining is in particular performed by grinding, trimming or milling and preferably controlled by a computer using CAD/CAM-based milling devices. This allows a so-called chair-side treatment of the patient by the

It is a particular advantage of the lithium metasilicate glass ceramic according to the invention that it can be shaped by machining without the undue wear of the tools observed with the tough and high-strength prior art materials. This is in particular shown by the easy possibility to polish and trim the glass ceramics according to the invention. Such polishing and trimming processes therefore require less energy and less time to prepare an acceptable product having the form of even very complicated dental restorations.

Further, the lithium metasilicate glass ceramic according to the invention can advantageously be processed to a lithium disilicate glass ceramic of high strength, which usually has a content of 50 to 85 vol. % and preferably 65 to 80 vol. % of crystalline lithium disilicate phase.

This is preferably effected by a process wherein the prepared lithium metasilicate glass ceramic of step (c) is subjected to a third heat treatment at a third temperature of 830 to 880° C. for a period of 10 to 60 minutes. This heat treatment can also be effected when hot-pressing the lithium metasilicate glass ceramic to achieve a shaping.

Thus, the lithium metasilicate glass ceramic can be further processed to the lithium dilsilicate glass ceramic of desired shape e.g. by both (i) CAD/CAM and a heat treatment or (ii) a hot-pressing. This is very advantageous for the user.

It is also possible to use for these purposes a corresponding lithium silicate glass which comprises nuclei suitable for formation of lithium metasilicate crystals. This glass is a precursor of the lithium metasilicate glass ceramic and the lithium disilicate glass ceramic of the invention. The invention is also directed to such a glass. It is obtainable by the above process in step (b). This lithium silicate glass according to the invention comprises the following components:

0 _	Component	wt%
	SiO_2	64.0 to 75.0, in particular 64.0-73.0
	Li ₂ O	13.0-17.0
	K_2O	2.0-5.0
	$A1_2O_3$	0.5-5.0
	Nucleating agent	2.0-5.0
5	Me(II)O	0-3.0

with Me(II)O being selected from at least one of CaO, BaO, MgO and SrO, and which comprises less than 0.1 wt. % of ZnO, and comprises nuclei suitable for formation of lithium metasilicate crystals.

For manufacturing a dental restoration by the hot pressing 5 technique, it is preferred to use a lithium silicate glass ingot according to the invention having nuclei for lithium metasilicate. This ingot is heated to about 700 to 1200° C. to convert it into a viscous state. The heat treatment can be conducted in a special furnace (EP 500®, EP 600®, Ivoclar Vivadent AG). The ingot is embedded in a special investment material. During the heat treatment the ingot will be crystallized. The main crystal phase is then lithium disilicate. The viscous glass ceramic flows under a pressure of 1 $_{15}$ to 4 MPa into the cavity of the investment material to obtain the desired shape of the dental restoration. After cooling the investment mould to room temperature the lithium disilicate restoration can be divested by sand blasting. The restoration can be further coated with a glass or a glass ceramic by 20 heat treatment. The obtained glass ceramics were then sintering or a hot pressing technique to obtain the finalized dental restoration with natural aesthetics.

The same hot-pressing technique can be applied to the lithium metasilicate glass ceramic according to the invention which will be converted to lithium disilicate glass ceramic. 25

A preferred method for converting the lithium metasilicate glass ceramic according to the invention to a lithium disilicate glass ceramic dental restoration by the CAD/CAM technique uses lithium metasilicate glass ceramic blanks, e.g. blocks, having a strength of about 80 to 150 Mpa. These can be easily machined in a CAM unit like Cerec 2® or Cerec 3® (Sirona, Germany). Larger milling machines such as DCS precimill® (DCS, Switzerland) are also suitable. The block is therefore positioned in the grinding chamber by a fixed or integrated holder. The CAD construction of the 35 dental restoration is done by a scanning process or an optical camera in combination with a software tool. The milling process needs for one unit about 10 to 15 minutes. Copy milling units such as Celay® (Celay, Switzerland) are also suitable for machining the blocks. First, a 1:1 copy of the 40 desired restoration is fabricated in hard wax. The wax model is then mechanically scanned and 1:1 mechanically transmitted to the grinding tool. The grinding process is therefore not controlled by a computer. The milled dental restoration has to be subjected to the third heat treatment to obtain the 45 desired lithium disilicate glass ceramic with high strength and tooth-like color. The product can be further coated with a glass or a glass ceramic by sintering or hot pressing technique to obtain the final dental restoration with natural aesthetics.

The lithium metasilicate glass ceramic according to the invention can also be used for coating a dental restoration. The coating is preferably effected by hot-pressing the lithium metasilicate glass ceramic onto the restoration.

It was surprisingly found that the easily machinable 55 lithium metasilicate glass ceramic according to the invention can be converted by a further heat treatment into a lithium disilicate glass ceramic product having also excellent optical properties. The conversion to a lithium disilicate glass ceramic is associated with a very small linear shrinkage of 60 only about 0.2 to 0.3%, which is almost negligible in comparison to a linear shrinkage of up to 30% when sintering ceramics. The obtained lithium disilicate glass ceramic has not only excellent mechanical properties, such as high strength, but also displays other properties required 65 for a material for dental restorations. It is emphasized that these properties are achieved without the need for ZnO as a

8

component which may be detrimental for specific restorations in view of its strong opalescent effect.

Thus, a product is finally obtained which has all the beneficial mechanical, optical and stability properties making lithium disilicate ceramics attractive for use as dental restorative materials. However, these properties are achieved without the disadvantages of the conventional materials when shaped by using a CAD/CAM based process, in particular the undue wear of the milling and trimming tools.

The invention is explained in more detail below on the basis of Examples.

EXAMPLES

Examples 1 to 8

A total of 8 different lithium metasilicate glass ceramics according to the invention with the chemical compositions given in Table I were prepared using the indicated second converted to the corresponding lithium disilicate glass ceramics using the indicated third heat treatment.

Firstly, samples of the corresponding starting glasses were melted in a platinum-rhodium crucible at a temperature of 1450° C. and for a period of 40 minutes. The glass melt was poured into water and the obtained granules were, after drying, again melted at 1500° C. The glass melts obtained were then poured into graphite moulds to give blocks. After relaxation of the glass blocks at 500 to 600° C. for 10 minutes to 3 hours, they were subjected to the given second heat treatment. Before effecting the third heat treatment, the blocks were checked for their machinability by milling in a CAD-CAM milling machine (i.e. CEREC 3®). Finally, the indicated third heat treatment was conducted. The crystal phases present after the second and third heat treatment were identified by XRD techniques and are given in table I.

Further, the opalescence of the products was visually assessed and the contrast value CR was determined according to BS 5612 (British Standard) using a spectral colorimeter (Minolta CM-3700d). The chemical stability in acetic acid was determined as well as the stability in artificial saliva. The corresponding data are to be found in the following Table II and show in particular the surprising combination of a lack of opalescence together with a high translucence and stability. The composition of the artificial saliva is given in table III.

The data obtained show that the lithium metasilicate glass ceramics according to the invention combine a very good machinability and high edge strength with the easy possibility to convert them by a simple heat treatment into lithium disilicate glass ceramics which have a very high bending strength as well as an excellent chemical durability and good translucence, all of which being properties which make them very attractive as materials useful for the manufacture of dental restorations.

Examples 9 to 12

Four glass ceramics according to the invention were prepared in analogous manner as examples 1 to 8. However, the heat treatment scheme was different. In addition each material was subjected to the schemes referred to as "Cycle A" and "Cycle B" which differ in the temperature used for the crystallization of lithium metasilicate, namely 650° and 700° C., respectively.

Details as to the materials prepared and tested as well as their properties are given in the table IV. It is apparent that the "Cycle B" treatment using a temperature of 700° C. for the crystallization of lithium metasilicate leads to lithium disilicate glass ceramics having excellent strengths.

9

TABLE I

	Example							
	1	2	3	4	5	6	7	8
Molar ratio	=							
SiO2:Li2O AI2O3:K2O	2.39:1 1:1.0	2.39:1 1:1.0	2.4:1 1:1.2	2.39:1 1:1.20	2.39:1 1:1.35	2.39:1 1:1.50	2.39:1 1:1.70	2.39:1 1:1.30
	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)	wt% (Mol %)
SiO2 K2O Li2O A12O3 P2O5 ZrO2 CeO2 V2O5 MnO2 Er2O3 MgO CaO Crystalline phases after:	72.21 (66.12) 3.16 (1.85) 14.99 (27.60) 3.45 (1.86) 3.28 (1.27) 2.91 (1.30)	70.64 (65.62) 3.09 (1.83) 14.68 (27.43) 3.38 (1.85) 3.21 (1.26) 3.00 (1.36) 1.88 (0.61) 0.12 (0.04)	70.52 (65.52) 3.81 (2.26) 14.64 (27.35) 3.35 (1.83) 3.2 (1.26) 2.5 (1.13) 1.86 (0.60) 0.12 (0.04)	70.78 (65.57) 3.76 (2.22) 14.7 (27.38) 3.38 (1.85) 3.21 (1.26) 1.8 (0.81) 2.00 (0.65) 0.07 ((0.02) 0.03 (0.02) 0.12 (0.017) 0.15 (0.21)	70.78 (65.56) 3.96 (2.34) 14.7 (27.38) 3.18 (1.74) 3.21 (1.26) 1.8 (0.81) 2.00 (0.65) 0.07 ((0.02) 0.03 (0.02) 0.12 (0.017) 0.15 (0.21)	70.78 (65.56) 4.16 (2.46) 14.7 (27.37) 2.98 (1.63) 3.21 (1.26) 1.80 (0.81) 2.00 (0.65) 0.07 ((0.02) 0.03 (0.02) 0.12 (0.17) 0.15 (0.21)	70.78 (65.55) 4.36 (2.58) 14.7 (27.37) 2.78 (1.52) 3.21 (1.26) 1.8 (0.81) 2.00 (0.65) 0.07 (0.02) 0.03 (0.02) 0.12 (0.017) 0.15 (0.21)	70.78 (65.29) 3.36 (1.98) 14.7 (27.26) 2.78 (1.51) 3.21 (1.25) 1.8 (0.81) 2.00 (0.65) 0.07 (0.02) 0.03 (0.02) 0.12 (0.017) 0.15 (0.21) 1.00 (0.99)
Second heat treatment: 20'/650° C.	Li2SiO3 Li2Si2O5 *	Li2SiO3 Li2Si2O5 *	Li2SiO3	Li2SiO3		Li2SiO3	Li2SiO3	Li2SiO3 Li2Si2O5
Third heat treatment: 10//850° C.	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*	Li2Si2O5 Li3PO4*

30

TABLE II

	Example					
	1	2	3	4	6	
CR-Value BS-	40.4	37.0	50.0	59.3	58.8	
5612 (1978)						
Opalescence	No	No	No	No	No	
Chemical stability	9	18	48	3	9	
in Acetic acid						
(24 h/80° C., mass						
loss in μg/cm ²)						
Chemical stability	13	17	28	27	17	
in Saliva						
(7 d/60° C., mass						
loss in μg/cm ²)						

TABLE III

Component	Amount in mg in a total of 500 ml H ₂ O
NaC1	125.64
KC1	963.9
NH ₄ Cl	178.0
CaCl ₂ •2H ₂ O	227.8
KSCN	189.2
$CO(NH_2)_2$	200.0
Na ₂ SO ₄ •10H ₂ O	336.2
NaHCO ₃	630.8
KH ₂ PO ₄	654.5

TABLE IV

10

		Example							
2.5		9	10	11	12				
35	SiO ₂	74.37	72.89	72.21	71.40				
	$K_2\tilde{O}$	3.26	3.18	3.16	3.13				
	Li ₂ O	15.44	15.13	14.99	14.79				
	$\overline{\text{A1}_2\text{O}_3}$	3.55	3.48	3.45	3.41				
	P_2O_5	3.38	3.31	3.28	3.22				
40	ZrO_2	0.00	2.01	2.91	4.05				
40	-		All values ab	ove in wt%					
	SiO ₂ :Li ₂ O	2.39	2.40	2.39	2.40				
	(Molratio %)								
	Cycle A:	(1) 500	° C./10 min +	(2) 650° C./20	min +				
			(3) 850° C	./10 min *)					
	Biaxial	786 +/- 92	515 +/- 54	522 +/- 82	479 +/- 36				
45	Flexural								
	Strength/MPa								
	Contrast Ratio	0.80	0.56	0.43	0.36				
	Cycle B:	(1) 500	° C./10 min +	(2) 700° C./20	min +				
			(3) 850° C	./10 min *)					
	Biaxial	828 +/- 104	659 +/- 75	608 +/- 90	694 +/- 113				
50	Flexural								
	Strength/MPa								
	Contrast Ratio	0.83	0.63	0.53	0.41				

^{*) (1)} Nucleation in the glass (2) Crystallization of Li-Metasilicate (3) Crystallization of Li-Disilicate from Li-Metasilicate

What is claimed:

- 1. A lithium silicate glass ceramic for dental restorations which comprises a main crystalline phase comprising lithium metasilicate, wherein the lithium metasilicate crystals comprise lamellar or platelet crystals, and wherein the molar ratio of SiO_2 to $\mathrm{Li}_2\mathrm{O}$ is at least 2.2:1.
- 2. The lithium silicate glass ceramic of claim 1, wherein the lithium metasilicate forms more than 50 and up to 80 vol.
 65 % of the lithium silicate glass ceramic.
 - 3. The lithium silicate glass ceramic of claim 1, wherein the glass ceramic is in form of a blank or a dental restoration.

12

4. The lithium silicate glass ceramic of claim **3**, wherein the blank is shaped into a dental restoration by machining or pressing.

11

- 5. The lithium silicate glass ceramic of claim 4, wherein machining comprises grinding, trimming or milling.
- 6. The lithium silicate glass ceramic of claim 4, wherein the dental restoration is an inlay, an onlay, a bridge, an abutment, a facing, a veneer, a facet, a crown, a partial crown, a framework or a coping.
- 7. The lithium silicate glass ceramic of claim 1, comprising SiO₂, Li₂O and a nucleating agent.
 - **8**. A lithium silicate glass ceramic material formed by:
 - a) heating a starting glass material which is essentially free of ZnO and comprises SiO₂, LiO₂, K₂O, Al₂O₃, nucleating agent, and optionally Me(II)O, wherein 15 Me(II)O is CaO, BaO, MgO, SrO or combinations thereon, in a first temperature range for a period of time such that nuclei suitable to form lithium metasilicate crystals are formed; and
 - b) heating the material from a) in a second temperature 20 range, which is higher than the first temperature range for a period of time to produce lithium silicate glass ceramic which has lithium metasilicate as the main crystalline phase, and wherein the crystals are of lamellar or platelet form.
- **9**. The lithium silicate glass ceramic of claim **8**, wherein the material formed after step b) is convertible to a lithium silicate glass ceramic having disilicate as the main crystalline phase by heating to a third temperature which is higher than the second temperature.

* * * * *